"A New Class of Organo-Tin Compounds containing Halogens." By William J. Pope, F.R.S., Professor of Chemistry, Municipal School, Manchester, and Stanley J. Peachey. Received April 20,—Read May 14, 1903.

(From the Chemical Laboratories, Municipal School of Technology, Manchester.)

Most of the organo-tin compounds which have hitherto been described may be regarded as derived from the hypothetical stanni-methane, $Sn H_4$, and, adopting a nomenclature based upon the name of this substance, the simple types of known organo-tin compounds may be described as the tetralkylstannimethanes, the trialkylstannimethyl chlorides, bromides and iodides, and the dialkylstannimethylene chlorides, bromides and iodides. The analogy between the various classes of derivatives of stannimethane and of methane is as yet incomplete in that no organo-tin compounds corresponding in constitution to chloroform, bromoform and iodoform have been described; methods for preparing such derivatives are, however, given in the present paper, so that the analogy of constitution existing between the corresponding classes of alkyl and halogen compounds of carbon and tin is shown to be complete, and of the kind illustrated by the following table.

$C(CH_3)_4$.	Tetramethylmethane.	$Sn(CH_3)_4$.	Tetramethylstanni-methylmethane.
$C(CH_3)_3I$.	Trimethylmethyl iodide.	$Sn(CH_3)_3I$.	Trimethylstannimethyl iodide.
$C(CH_3)_2I_2$.	Dimethylmethylene iodide.	$Sn(CH_3)_2I_2$.	Dimethylstannimethylene iodide.
$C(CH_3)I_3$.	Methyliodoform.	$Sn(CH_3)I_3$.	Methylstanniodoform.
CI_4.	Carbon tetriodide.	SnI_4.	Stannic iodide.
$CH_3.CO.OH$.	Acetic acid.	$CH_3.SnO.OH$.	Methylstannoxylic acid.

Methylstanniodoform, $CH_3.SnI_3$.

Since tetramethylstannimethane is acted upon by iodine with production of trimethylstannimethyl iodide and methyl iodide in accordance with the following equation—

$$Sn(CH_3)_4 + I_2 = Sn(CH_3)_3I + CH_3I,$$
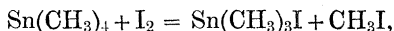
it seemed not unlikely that, on replacing the iodine by stannic iodide, the reaction would take the course indicated by the following equation—

$$Sn(CH_3)_4 + SnI_4 = Sn(CH_3)_3I + Sn(CH_3)I_3.$$
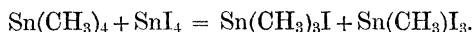
This was found to be the case.

On warming a mixture of tetramethylstannimethane (two parts) and stannic iodide (seven parts) on the water bath, the iodide rapidly dissolves

and, after a few hours standing at the ordinary temperature, methylstanni-iodoform crystallises in large straw-coloured prisms; the separation of the latter is rendered more complete by the addition of petroleum ether, and, after filtration, the stanniodoform derivative is purified by crystallisation from ether or light petroleum. It crystallises in long needles or prisms closely resembling iodoform in colour and melts at 82—84°; it gradually volatilises at 100° and, when slowly heated, distils without decomposition. It is odourless and dissolves very readily in alcohol, acetone and benzene. The following analytical results were obtained :—

0·3083 gave 0·0254 CO_2 and 0·0172 H_2O.   C = 2·24.   H =   0·62.
0·2964 required 17·5 × 0·0169 $AgNO_3$ for titration.   I = 74·4.

Theory for $Sn(CH_3)I_3$.   C = 2·33.   H = 0·58.   I = 74·0.

Methylstannoxylic Acid, $CH_3.SnO.OH$.

Methylstanniodoform is insoluble in cold water, but dissolves in boiling water giving a solution from which the iodoform derivative cannot subsequently be crystallised; as this behaviour should be attributable to the occurrence of hydrolysis in the following sense, $CH_3.SnI_3 + 3H_2O = CH_3.Sn(OH)_3 + 3HI$, methylstanniodoform was evaporated on the water bath with an aqueous solution of three molecular proportions of soda; as evaporation proceeded a white precipitate of methylstannoxylic acid was deposited, the reaction being represented by the following equation :—

$$CH_3.SnI_3 + 3NaHO = CH_3.SnO.OH + 3NaI + H_2O.$$

After washing with water, solution in acetic acid and precipitation with ammonia, the substance gave the following analytical results :—

0·3887 gave 0·0990 CO_2 and 0·0822 H_2O and 0·3532 SnO_2. C = 6·94.
H = 2·36.   Sn = 71·60.
0·3396 gave 0·0869 CO_2, 0·0800 H_2O and 0·3024 SnO_2. C = 6·97.
H = 2·63.   Sn = 70·16.
$CH_3.SnOOH$ requires C = 7·18.   H = 2·41.   Sn = 71·24.

By the action of methyl iodide on sodium stannite, G. Meyer[*] obtained a white powder in which he made one determination of tin, and which he considered to be probably the acid which we now describe. On repeating Meyer's preparation we found that the substance obtained is identical with the methylstannoxylic acid prepared from methylstanniodoform. To the very scanty description given by Meyer we would add the following.

The acid is conveniently prepared by dissolving stannous chloride

[*] 'Berichte,' vol. 16, p. 1439.

(100 grams) in the minimum quantity of water, and adding concentrated caustic soda solution until the precipitate formed at first just redissolves. To the solution thus obtained (300 c.c.), absolute alcohol (200 c.c.) and methyl iodide (90 grams) are added; the liquid becomes warm and, after two days repose at the ordinary temperature, is saturated with carbon dioxide, filtered and evaporated on the water bath. During the evaporation, methylstannoxylic acid separates in white crystalline crusts and is obtained in a practically pure condition after filtration and washing with boiling water. The acid is insoluble in water and the ordinary organic solvents, but dissolves slowly in boiling acetic and formic acids. On adding ammonia to the acetic acid solution after dilution with water, no precipitate forms, but on boiling, methylstannoxylic acid separates in a state of purity; the fact that no precipitate occurs until the solution is boiled, indicates the existence in solution of an ortho-acid $CH_3.Sn(OH)_3$, which is only decomposed on heating. Methylstannoxylic acid decomposes slowly at 120—130°, but no volatile tin compound is evolved; on rapid heating it chars and, when ignited, smoulders leaving a residue of stannic oxide. On boiling the acid with dilute caustic potash the greater part dissolves, but the solution never becomes quite clear; when the acid is boiled with stronger potash solution, a rapid evolution of methane occurs, a sublimate of trimethylstannicarbinol, $(CH_3)_3Sn.OH$, forms and the solution is afterwards found to contain dimethylstannimethylene oxide $(CH_3)_2SnO$. Lastly, on mixing the acid with solid potash and heating, after the addition of a small quantity of water, methane containing a considerable proportion of tetramethylstannimethane is given off; the latter substance was identified by freezing it out of the gas and determining its boiling point and behaviour towards iodine. The fact that methylstannoxylic acid is not wholly soluble in dilute potash is attributable to a part of it being decomposed with evolution of methane and production of stannic oxide which remains undissolved by the potash. The evolution of methane which attends the heating of methylstannoxylic acid with potash, is quite analogous to the decomposition which occurs when sodium acetate is heated with soda-lime, whilst the formation of dimethylstannimethylene oxide is analogous to the production of acetone by heating calcium acetate; it is, however, difficult to find analogies for the formation of trimethylstannimethyl alcohol and tetramethylstannimethane during the heating of the stannoxylic acid with potash. The four kinds of change would seem to take place in accordance with the following equations:—

(1.) $CH_3.SnO.OH = CH_4 + SnO_2.$
(2.) $2CH_3.SnO.OH = (CH_3)_2SnO + SnO_2 + H_2O.$
(3.) $3CH_3.SnO.OH = (CH_3)_3Sn(OH) + 2SnO_2 + H_2O.$
(4.) $4CH_3.SnO.OH = (CH_3)_4Sn + 3SnO_2 + 2H_2O.$
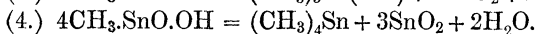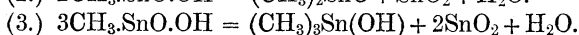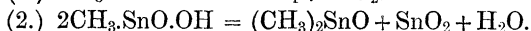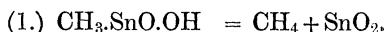
Equation (2) is similar to that suggested by Pfeiffer,* in order to explain the fact that he obtained diethylstannimethylene oxide instead of ethylstannoxylic acid by the action of ethyl iodide on sodium stannate.

A number of attempts were made to prepare salts of methylstann-oxylic acid, but these have been uniformly unsuccessful owing to the very feebly marked acidic characters of the substance. The acidic properties of methylstannoxylic acid are, in fact, so very slight that the substance tends to react in the ortho-form rather than in the stannoxylic condition, although the reverse is true in the case of carboxylic acids. Thus, on treating methylstannoxylic acid with concentrated hydriodic acid, it is immediately converted into methyl-stanniodoform, so that the reaction, by means of which we first pre-pared the acid, is a reversible one; since methylstannoxylic acid is very easily prepared in quantity by the action of methyl iodide on alcoholic sodium stannite solution, the most convenient method of preparing the stanniodoform derivative consists in treating methyl-stannoxylic acid with strong hydriodic acid, and, after filtration, crystallising the product from a mixture of benzene and light petroleum.

Methylstannibromoform, $CH_3.SnBr_3$.

Methylstannoxylic acid dissolves readily in concentrated hydro-bromic acid, and on extracting the solution with light petroleum and evaporating the solvent, methylstannibromoform separates. After crystallisation from petroleum it is obtained in the form of long colourless prisms which melt at 50—55° and may be distilled without decomposing. The substance fumes slightly in the air and dissolves to a clear solution in water. Methylstannibromoform is readily soluble in the ordinary organic solvents. The following analytical results were obtained:—

0·4664 gave 0·0563 CO_2 and 0·0382 H_2O.   C = 3·29.   H = 0·91.
$CH_3.SnBr_3$ requires C = 3·21 and H = 0·80.

Methylstannichloroform, $CH_3.SnCl_3$.

Methylstannoxylic acid dissolves in concentrated hydrochloric acid with evolution of heat, and, after saturating the solution with anhydrous calcium chloride and extracting with benzene, the benzene solution yields a residue when evaporated which slowly crystallises in the desiccator. On gently warming methylstannoxylic acid in a current of dry hydrogen chloride, reaction occurs and methylstannichloroform distils, condensing in the receiver as a colourless crystalline material.

* 'Berichte,' vol. 35, p. 3303.

The same product is formed on treating the acid with phosphorus trichloride. Methylstannichloroform crystallises from light petroleum in long colourless prisms melting at 105—107° and distils without decomposition at 179—180°. It fumes in the air, dissolves to a clear solution in water, and is very soluble in the ordinary organic solvents.

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" On the Photo-electric Discharge from Metallic Surfaces in different Gases." By W. Mansergh Varley, M.Sc. (Vict.), Ph.D. (Strasburg), 1851 Exhibition Research Scholar, Emmanuel College, Cambridge. Communicated by Professor J. J. Thomson, F.R.S. Received April 24,—Read May 14, 1903.

(Abstract.)

The object of the experiments described in this paper was to study as systematically as possible the effect of the pressure and nature of the gas with which a metal surface is surrounded upon the magnitude of the photo-electric current from the surface.

On account of the complicated nature of the relation between the photo-electric current and the potential difference between the electrodes, it is not enough to state, for example, that the current in air at 760 mms. pressure is so many times that in air at 50 mms. pressure, without specifying the exact conditions under which the observations were taken. The method used in these experiments was to draw the complete curves connecting the current and the potential difference at each pressure examined, keeping the intensity of the ultra-violet illumination and the other conditions unaltered.

Great difficulty was encountered in finding a suitable source of ultra-violet light which would remain constant in intensity while long series of observations were being taken, but ultimately the spark between iron terminals in an atmosphere of pure dry hydrogen was found to answer excellently. The spark gap was in parallel with three Leyden jars in the secondary circuit of an induction coil, used as a transformer.

The photo-electric currents were measured from a metal—usually zinc—surface placed a few millimetres behind a fine gauze, through which the light passed, and which served as the positive electrode. A brass vessel, with a quartz window to admit the light, served to contain the electrodes. It was connected to pump, gauge, &c., so that the pressure or gas could be changed at will.

A second similar apparatus was used as a control for the intensity of the light.